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Pyrolysis gas chromatography/mass spectrometry identification of poly(butadiene-acrylonitrile) rubbers

John A. Hiltz *

Defence Research Establishment Atlantic, Dockyard Laboratory, Building D-17, P O Box 99000, Station Forces, Halifax, NS, Canada B3K 5X5

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Abstract

Pyrolysis (py) coupled with gas chromatographic (GC) separation and mass spectrometric (MS) detection is routinely used to identify intractable polymers including cross-linked rubbers. For some rubbers, such as natural rubber, the major thermal degradation pathways and degradation products are known. The presence of the characteristic degradation products in the pyrolysate is sufficient to positively identify the rubber Unambiguous identification of other rubbers is more difficult. For instance copolymer rubbers such as poly(butadiene-acrylonitrile) release degradation products from the butadiene rich areas, acrylonitrile rich areas, and areas in the rubber where butadiene and acrylonitrile are adjoined Degradation products such as ethenylcyclohexene (the dimer of butadiene) and acrylonitrile are characteristic of poly(butadiene-acrylonitrile) rubbers but not unique to them. In this paper a pyrolysis gas chromatographic/mass spectrometric (py-GC/MS) method for the identification of poly(butadiene-acrylonitrile) rubbers is described. The method is based on the identification of compounds in the pyrolysate that can be attributed to areas of the copolymer rubber where acrylonitrile and butadiene molecules are adjoined As these are unique to the pyrolytic degradation of poly(butadiene-acrylonitrile) copolymer rubbers they allow positive identification of these rubbers. © 2000 Elsevier Science B V All rights reserved

Keywords: Pyrolysis, Pyrolysis-gas chromatography/mass spectrometry (py-GC/MS), Poly(butadiene-acrylonitrile) rubber, NBR, Identification

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1. Introduction

Poly(butadiene-acrylonitrile) or NBR rubber, which is commonly used for gaskets and o-rings in fuels systems, is specified for use as fuel system gasketing onboard Canadian Forces Naval vessels. However, at the shop floor level there is often concern about whether the elastomer received from stores is in fact NBR rubber. This concern is well founded as the use of an elastomer without the required fuel resistance results in gasket degradation and the potential of fuel leaks. Fuel leaks pose a serious fire hazard.

Our laboratory is often asked to confirm the identity of gasket material prior to installation in ships' fuel systems. The classic approach for the identification of elastomers involves sodium fusion to determine the presence of elements such as nitrogen, sulfur and halogens followed by specific chemical tests [1]. However, there is no specific test for NBR rubber. That is, negative results for polyurethane and vinylpyridine rubber tests are interpreted as a positive test for NBR rubber. Ideally, the analyst would like a technique that allowed the positive identification of a NBR rubber.

Pyrolysis gas chromatography (py-GC) and pyrolysis gas chromatography/mass spectrometry (py-GC/MS) have been used to identify a broad range of polymeric materials [2–11]. Pyrolysis provides a reproducible means of thermally degrading polymeric materials while capillary gas chromatography coupled with mass spectrometric detection separate and identify the complex mixture of degradation products. As the manner in which a material degrades is related to its structure, the degradation products provide a means of identifying polymeric materials.

Natural and poly(chloroprene) rubbers are examples of elastomers that are readily identified using py-GC/MS. The major thermal degradation pathways of these rubbers are known and from these the characteristic degradation products of these rubbers can be deduced. For both of these rubbers the preferred thermal degradation mechanism involves cleavage of the bond beta to the double bond. Further reaction leads to the formation of monomer, a cyclic dimer, and for natural rubber, compounds incorporating three and four monomer units.

The major degradation product of natural rubber is 1-methyl-4-(1-methylethenyl)cyclohexene [12]. The presence of this compound as the major degradation product along with 2-methyl-1,3-butadiene (monomer) and groupings of compounds containing 15 and 20 carbon atoms (three and four monomer) units in the pyrolysate of a rubber is sufficient to identify it as natural rubber. Similarly, the presence of 1-chloro-4-(1-chloroethenyl)cyclohexene and 2-chloro-1,3-butadiene, the cyclic dimer and monomer of poly(chloroprene) rubber, in the pyrolysate of a rubber identify it as poly(chloroprene) rubber.

The use of pyrolysis GC/MS to identify copolymer rubbers, such as NBR rubber, is more difficult. This difficulty arises from the fact that pyrolytic degradation products of NBR rubber arise from the butadiene or acrylonitrile rich areas of the rubber and areas where the butadiene and acrylonitrile molecules adjoin each other.

Alekseeva [13] reported that NBR rubbers could be identified on the basis of acrylonitrile, butadiene and ethenylcyclohexene in the pyrolysate. Our experience

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has been that acrylonitrile is difficult to identify in the pyrolysate of some NBR rubbers. Further, these compounds are not unique to NBR rubber. Hummel et al. [14] characterized a number of copolymer rubbers, including NBR rubber, using py-MS. They proposed a fragmentation scheme to account for many of the major ions in the mass spectrum of NBR rubber. In particular, the scheme accounted for ions from areas of the rubber with adjoining acrylonitrile and butadiene molecules.

In this paper the results of a py-GC/MS study to identify pyrolytic degradation products characteristic of and unique to NBR rubbers are reported. The study concentrated on identifying degradation products that could be attributed to areas of NBR rubber where butadiene and acrylonitrile molecules are adjoined. The fragmentation scheme proposed by Hummel et al. was used as a starting point for the identification of characteristic degradation products.

2. Experimental

2.1. Materials

Three vulcanized poly(butadiene-acrylonitrile) (NBR) rubbers were used in this study. The composition of two of the NBR rubbers, referred to as NBR #1 and NBR #2, are listed in Tables 1 and 2, respectively. No compositional data was available for the third rubber, referred to as NBR #3. It was received from Formation Halifax Stores and reported to be a Military Specification MIL R 6855D class 1 rubber. MIL R 6855D class 1 rubbers are butadiene-acrylonitrile rubbers. NBR #1 had a Shore Durometer A hardness of 60, NBR #2 had a Shore Durometer A hardness of 65, and NBR #3 had a Shore Durometer A hardness of 60.

Poly(butadiene) (98% *cis*) and poly(acrylonitrile) were purchased from Scientific Polymer Products (Ontario, NY). The poly(butadiene) had an approximate molecular weight of 200 000, a Mooney viscosity of 40, and a glass transition temperature (Tg) of -102°C. The poly(acrylonitrile) had an approximate molecular weight of 150 000, and a Tg of 85°C.

Table 1
Composition of poly(butadiene-acrylonitrile) rubber NBR #1

Component	Parts per hundred resin (phr)
Uniroyal paracril BJLT M-50 (33% acrylonitrile)	100
Zinc oxide	5
Stearic acid	0.5
Carbon black N330	18
TMTD (tetramethylthiuram disulfide)	3
Sulfur	0.5

Table 2
Composition of poly(butadiene-acrylonitrile) rubber NBR # 2

Component	Parts per hundred resin (phr)
Paracril 1880 (18% bound acrylonitrile rubber)	50
Breon 36-70 (36% bound acrylonitrile rubber)	50
Zinc oxide	5
Stearic acid	1
Nonox B	0.5
Sulfur	0.5
MBTS (2,2'-dithiobis(benzothiazole))	1
TMTM (tetramethylthiauram monosulfide)	0.5
Philblack SR (carbon black N770)	60
Dioctyl sebacate	6
Dutrex RT (aromatic oil)	4

2.2. Py-GC/MS

All pyrolyses were performed using a CDS Model 122 pyroprobe controller and a platinum coil pyroprobe (Chemical Data Systems, Oxford, PA). The rubber sample (0.1–0.2 mg) was centered with glass wool in a 25-mm quartz tube and heated with the ramp off (maximum heating rate) to the final temperature (600, 700, 800, or 900°C). The hold time at the final temperature was 20 s.

GC/MS analysis was carried out on a Fisons Platform II quadrupole GC/MS with a Fisons Model 8000 GC. The pyrolysis products were separated on a 30 m long × 0.25 mm inside diameter ARX-5 capillary column with a 0.25 μm thick stationary phase (5% phenyl-95% dimethylpolysiloxane). The GC was operated in the pressure control mode using Helium (linear flow rate 0.3 ms^{-1} at 40°C) as the carrier gas. To reduce deadspace between the pyroprobe and the head of the GC column, the column was threaded up through the pyroprobe interface and positioned adjacent to the end of the pyrolysis tube.

The GC oven was programmed to hold at 40°C for 4 min, then increase to 300°C at a rate of 10°C min^{-1}, and finally hold at 300°C for 10 min. The total run time was 40 min.

The quadrupole MS was operated in the full scan mode between 25 atomic mass units (amu) and 500 amu. The scan rate was 1 scan per s. Data acquisition and manipulation was performed on a MassLynx data system containing the NIST library of mass spectra (≈ 65 000 entries).

3. Results and discussion

3.1. Effect of pyrolysis temperature

The pyrograms of NBR # 1 samples following pyrolysis at 600, 700, 800, and

900°C are shown in Fig. 1. The number and relative concentration of pyrolytic degradation products changed slightly with pyrolysis temperature. For instance the intensities of peaks at 10.65 and 15.43 min decreased relative to the ethenylcyclohexene peak (5.72 min) as the pyrolysis temperature was increased from 600 to 900°C. This suggests that the compounds giving rise to the peaks at 10.65 and 15.43 min underwent further reactions as the pyrolysis temperature was increased. These might include cyclization and dehydrogenation to form aromatic compounds. The intensity of the toluene peak (3.73 min) increased relative to ethenylcyclohexene peak as the pyrolysis temperature was increased from 600 to 900°C. This is consistent with increased cyclization and dehydrogenation of the pyrolysate as the pyrolysis temperature is increased.

All subsequent pyrolyses in this paper were carried out at 700°C as this is the temperature we use to pyrolyse other elastomeric materials.

3.2. Selection of degradation products characteristic of NBR rubbers

The pyrograms of samples of *cis* poly(butadiene), poly(acrylonitrile) and NBR rubber are shown in Fig. 2.

The pyrogram of poly(butadiene) has a major peak at 5.68 min and groupings of peaks centered at 13.6, 19.0, and 23.5 min. Mass spectral analysis indicated that the

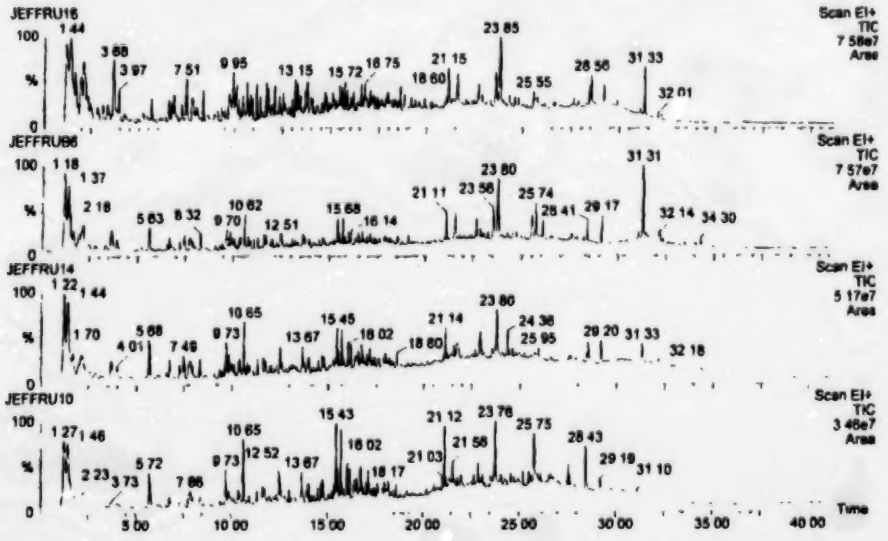


Fig 1 From top to bottom, pyrograms of NBR # 1 following pyrolysis at 900, 800, 700, and 600°C, respectively

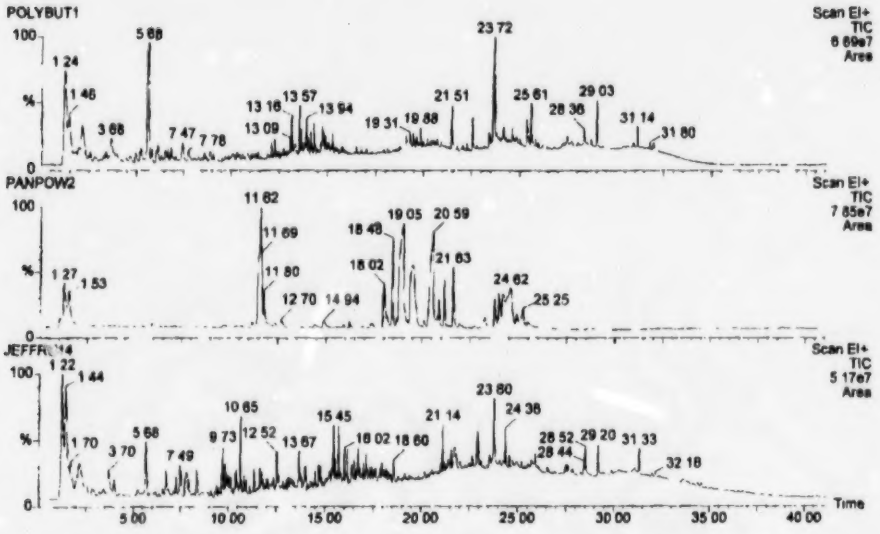


Fig 2 Pyrograms of (top) poly(butadiene), (middle) poly(acrylonitrile) and (bottom) NBR # 1 samples

peak at 5.68 min was ethenylcyclohexene and the groupings of peaks at 13.6, 19.0, and 23.5 min were hydrocarbons containing 12, 16, and 20 carbons, respectively. Ethylenecyclohexene is the cyclic dimer of 1,3-butadiene and the hydrocarbons containing 12, 16, and 20 carbons arise from fragments incorporating three, four and five 1,3-butadiene units, respectively.

The pyrogram of poly(acrylonitrile) consists of peaks at 1.27, 1.43, 11.62 min, and groups of peaks between 18 and 22 min, and 23.5 and 26 min. Mass spectral analysis of the peaks at 1.27, 1.43, and 11.62 min indicated they were acrylonitrile (2-propenenitrile), butenenitrile, the dimer of 2-propenenitrile (2-methylene-1,5-pentanedinitrile), respectively. Mass spectral analysis of the other peaks between 18 and 22 min suggested that they were degradation products resulting from three 2-propenenitrile units, and the peaks between 23.5 and 26 min from four 2-propenenitrile units. For instance mass spectral analysis of the peak at 18.02 min indicated it was tricyanobenzene ($C_9N_3H_3$). This was formed by the cyclization of three 2-propenenitrile units followed by dehydrogenation.

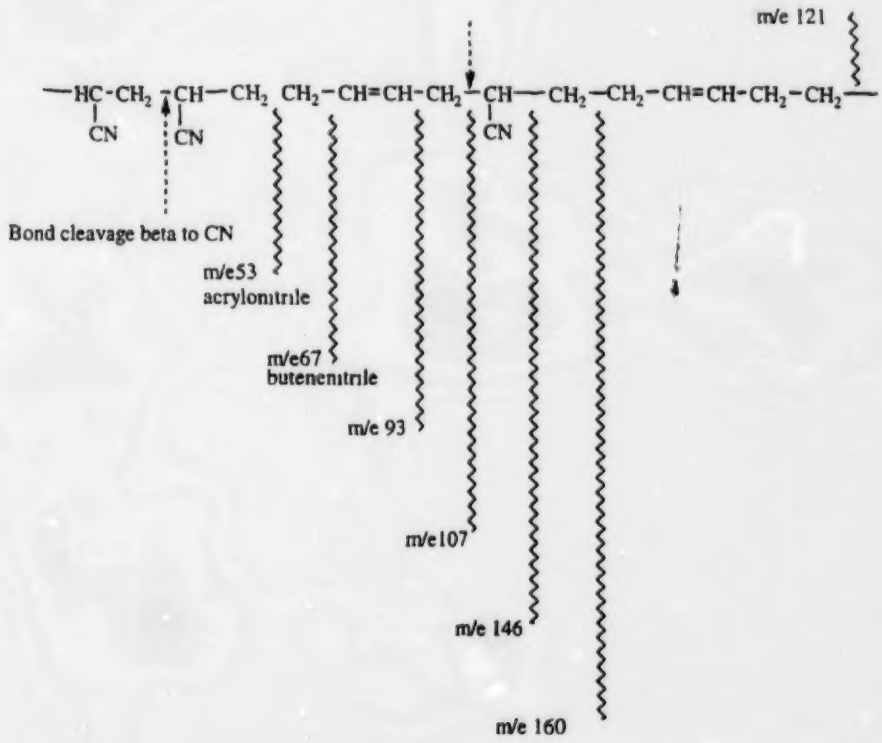
The pyrogram of the NBR rubber sample is significantly different from the pyrograms of the poly(butadiene) and poly(acrylonitrile). The major peak in the pyrogram of poly(acrylonitrile), 2-methylene-1,5-pentanedinitrile (11.62 min), was not present in the NBR rubber pyrogram. This suggests that there were few acrylonitrile-acrylonitrile segments in the NBR rubber. Ethenylcyclohexene (5.71 min), a major degradation product of poly(butadiene), was present in the NBR rubber degradation products but the groups of peaks corresponding to compounds containing 12, 16, and 20 carbons were difficult to identify. Degradation products that were not present in either the poly(butadiene) or poly(acrylonitrile) pyrograms,

specifically products that arise from segments of the rubber where butadiene and acrylonitrile molecules adjoin, were of more interest.

The NBR rubber pyrogram has a number of peaks with retention times between 8 and 16 min that are not present in the pyrograms of either poly(butadiene) or poly(acrylonitrile). If the compounds giving rise to these peaks can be related structurally to NBR rubber, then these can be used to identify NBR rubbers.

3.3. Identification of degradation products characteristic of a NBR rubber

A fragment of NBR rubber with adjoining acrylonitrile and butadiene molecules is shown in Scheme 1. Consideration of the bond strengths indicates that thermal cleavage takes place preferentially at tertiary carbon atoms and at bonds beta to (two bonds removed from) the CN triple bond [14]. Some of the major ions arising from the pyrolytic degradation of NBR rubber can be deduced and are shown in Scheme 1. The fragments with m/e 93, 107 and 160 contain atoms originally associated with both an acrylonitrile and a butadiene molecule. This suggested that compounds with molecular weights of 93, 107 and 160 and structures consistent



Scheme 1

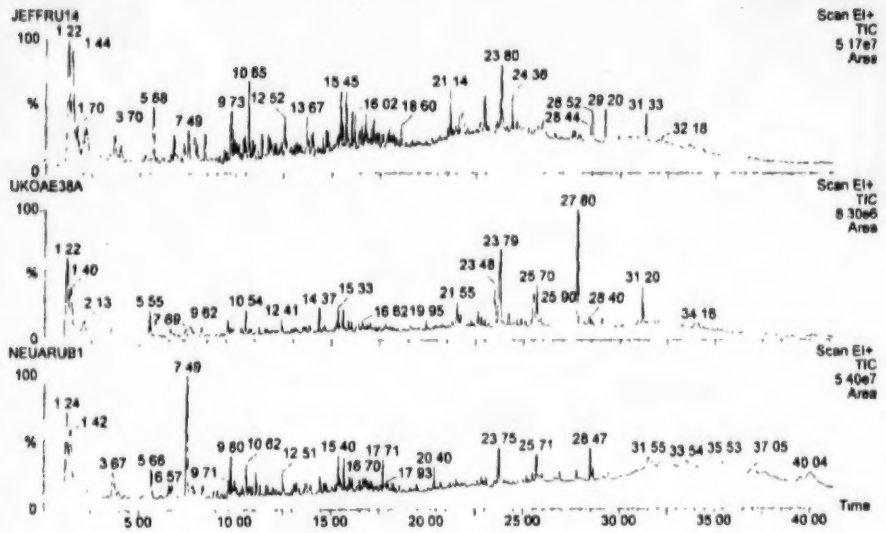


Fig 3 Pyrograms at 700°C of (top) NBR # 1, (middle) NBR # 2 and (bottom) NBR # 3 rubbers

with the fragments in Scheme 1 might be found in the pyrograms and could be used to identify NBR rubber.

The pyrograms of NBR rubbers NBR # 1, NBR # 2, and NBR # 3 are shown in Fig. 3. There are a number of degradation products that are common to the three NBR rubber samples. Some of these, such as ethenylcyclohexene ($\approx$ 5.6 min), are not unique to the pyrolytic degradation of NBR rubber. However, as was noted for NBR # 1, there were a number of compounds with retention times between 8 and 16 min that are unique to the NBR rubber samples. That is, the compounds were not found in the pyrograms of either poly(butadiene) or poly(acrylonitrile).

Fig. 4 shows an expansion of the NBR rubber pyrograms between 8 and 16 min. Mass spectral analysis of peaks with retention times between 8 and 16 min indicated compounds with molecular weights of 93 (8.3 min), 107 (10.6 min), and 160 (15.4 min) were indeed present in the pyrolysate. These peaks are numbered 1, 3, and 5 in Fig. 4. Two other compounds, peak 2 (9.89 min) and peak 4 (12.52 min) in Fig. 4, were selected as possible degradation products arising from areas of the rubber where acrylonitrile and butadiene molecules adjoin. The structure of these compounds, deduced from their mass spectra, are discussed below.

The mass spectra of the compound giving rise to peak 1 in the pyrograms of the three NBR rubber samples are shown in Fig. 5. The compound has a molecular weight of 93. A degradation product with a molecular weight of 93 was predicted in Scheme 1. The odd number molecular weight is indicative of a compound with an odd number of nitrogen atoms. The most intense ion is at m/e 66 and corresponds to a loss of m/e 27 from the molecular ion. Hydrogen cyanide (HCN) has a mass of 27 and is commonly lost from NBRs with labile hydrogen atoms. The

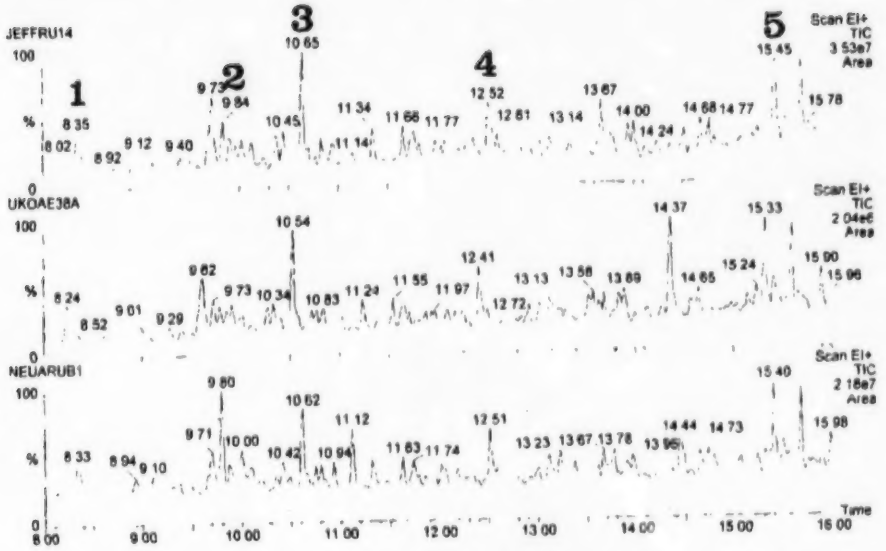


Fig 4 Expansion of pyrograms shown in Fig 3 between 8 and 16 min retention time

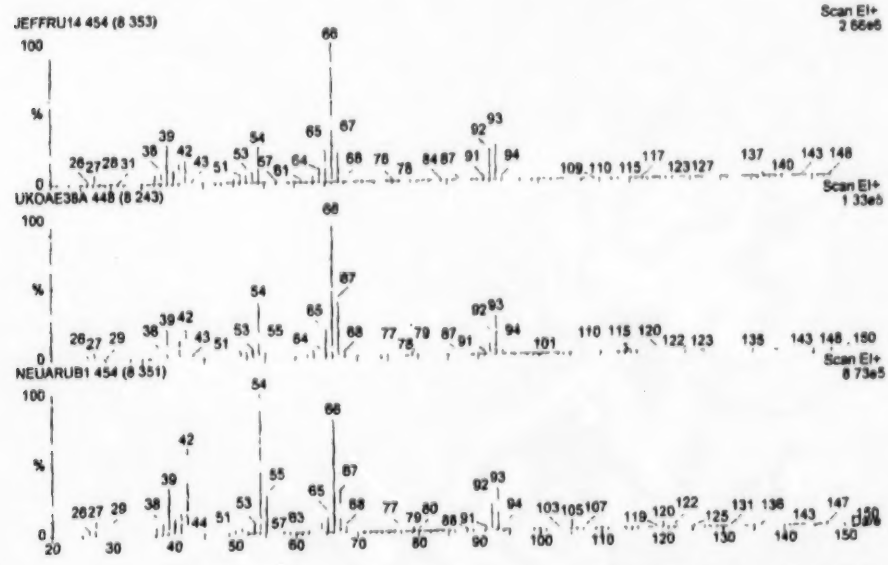
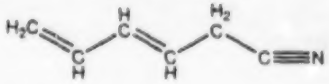


Fig 5 Mass spectra of the compounds giving rise to peak 1 in pyrograms of the three rubbers shown in Fig 4

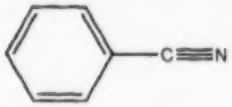
Possible Structure(s)

Peak # 1 MW 93. C6H7N



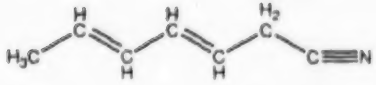
1-cyano-2,4-pentadiene

Peak #2 MW 103, C_7H_5N



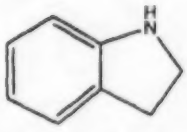
benzonitrile or cyanobenzene

Peak #3 MW 107,C_7H_9N

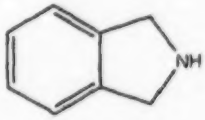


1-cyano-2,4-hexadiene

Peak #4 MW 119, C_8H_9N

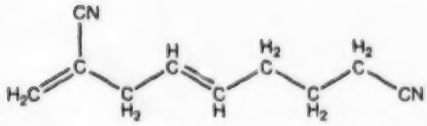


2,3-dihydroindole



1,3-dihydroisoindole

Peak #5 MW 160,$C_{10}H_{14}N_2$



1,7-dicyano-4,7-octadiene

Scheme 2

mass spectral library search indicated that the compound was an unsaturated NBR with the molecular formula C_6H_7N. A possible structure consistent with the mass spectrum and the proposed degradation pathways in Scheme 1 is shown in Scheme 2.

The mass spectra of the compound giving rise to peak 2 are shown in Fig. 6. The compound has a molecular weight of 103. The odd number molecular weight is indicative of a compound with an odd number of nitrogens. The two most intense

ions are the molecular ion (m/e 103) and an ion at m/e 76. The loss of m/e 27 from the molecular ion is characteristic of the loss of HCN and high intensity of the molecular ion is characteristic of aromatic nitriles. The mass spectral library search identified the compound as benzonitrile (C_7H_5N). Although the formation of benzonitrile is not predicted in Scheme 1, cyclization and dehydrogenation of the pyrolytic degradation product with a mass of 107 would result in the formation of this compound. A mechanism for the formation of benzonitrile is shown in Scheme 3

The mass spectra of the compound giving rise to peak 3 are shown in Fig. 7. The compound has a molecular weight of 107 and such a compound was predicted in Scheme 1. The odd number molecular weight is characteristic of compounds containing an odd number of nitrogen atoms. The ion at m/e 80 arises from the loss of m/e 27 from the molecular ion and is characteristic of the loss of HCN from the compound. A possible structure consistent with the mass spectrum and the degradation pathways in Scheme 1 is shown in Scheme 2.

The mass spectra of the compound giving rise to peak 4 are shown in Fig. 8. The compound has a molecular weight of 119. The odd number molecular weight indicates the compound has an odd number of nitrogen atoms. As was noted for peak 2, a compound with molecular weight 119 is not predicted in Scheme 1. However, further reaction (including cyclization and dehydrogenation) of the fragment with molecular weight 121 could result in a compound with a molecular weight of 119. The intense molecular ion peak suggests that the compound is aromatic, while the intense M-1 peak at 118 indicates the presence of an α-hydro-

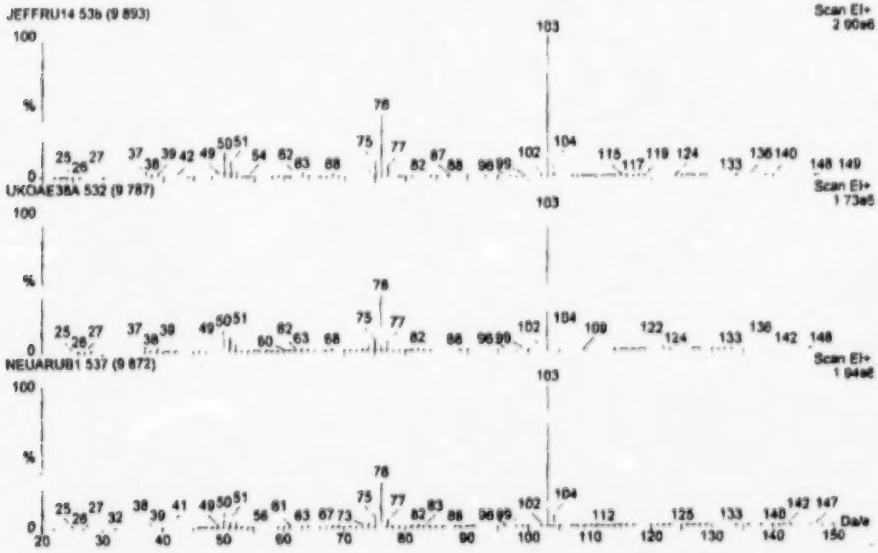
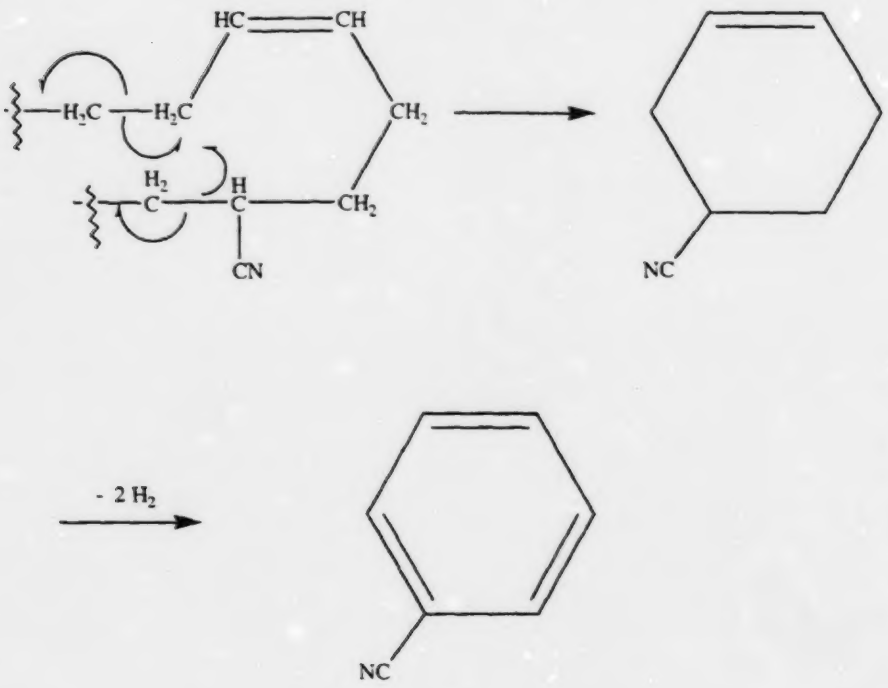


Fig 6 Mass spectra of the compounds giving rise to peak 2 in pyrograms of the three rubbers shown in Fig 4



Benzonitrile

Scheme 3

gen. A library search of mass spectrum indicated that the compound was 2,3-dihydroindole.

The mass spectra of the compound giving rise to peak 5 are shown in Fig. 9. The compound has a molecular weight of 160. This indicates that it either has no nitrogen atoms or an even number of nitrogen atoms. The peak at 133 is consistent with the loss of HCN, suggesting the compound contains at least two nitrogen atoms. The most intense ions are at m/e 67 and m/e 41. Common elemental compositions of these ions are C_4H_5N and C_2H_3N, respectively. A possible structure for this compound, consistent with the mass spectrum and the degradation pathways in Scheme 1, is shown in Scheme 2.

3.4. Unknown rubber

The pyrogram of an unknown rubber from a fuel hose is shown in Fig. 10. The application in which the rubber was used and the presence of butadiene in the pyrolysate suggested it might be NBR rubber. Mass spectral analysis of the peaks between 7 and 15 min indicated that the five compounds selected to characterize

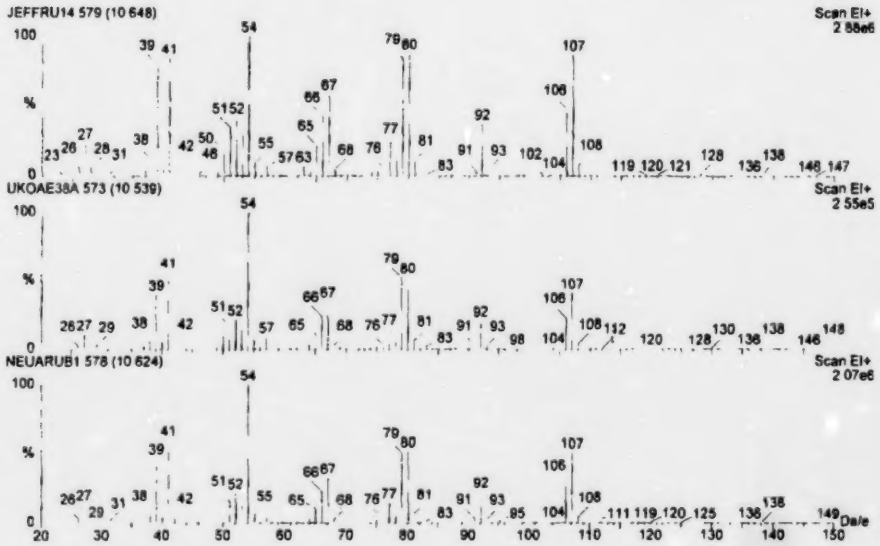


Fig 7 Mass spectra of the compounds giving rise to peak 3 in pyrograms of the three rubbers shown in Fig 4

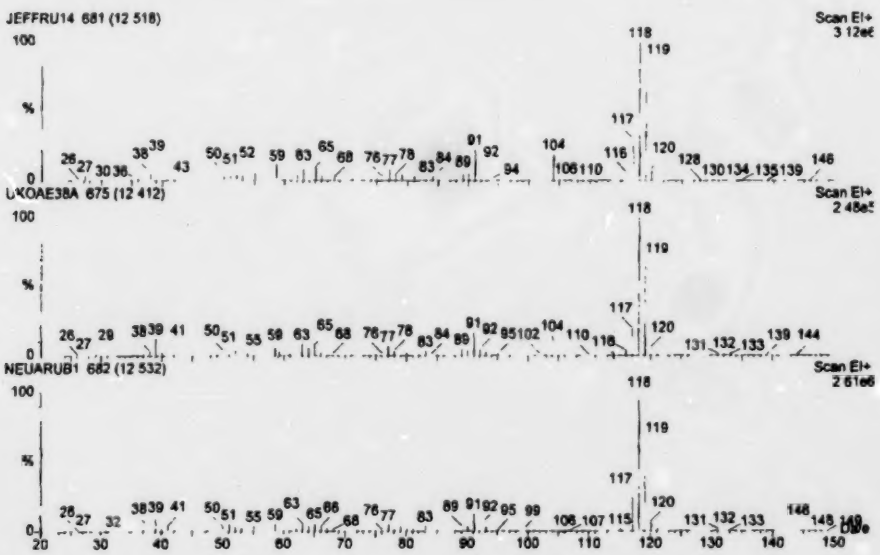


Fig 8 Mass spectra of the compounds giving rise to peak 4 in pyrograms of the three rubbers shown in Fig 4

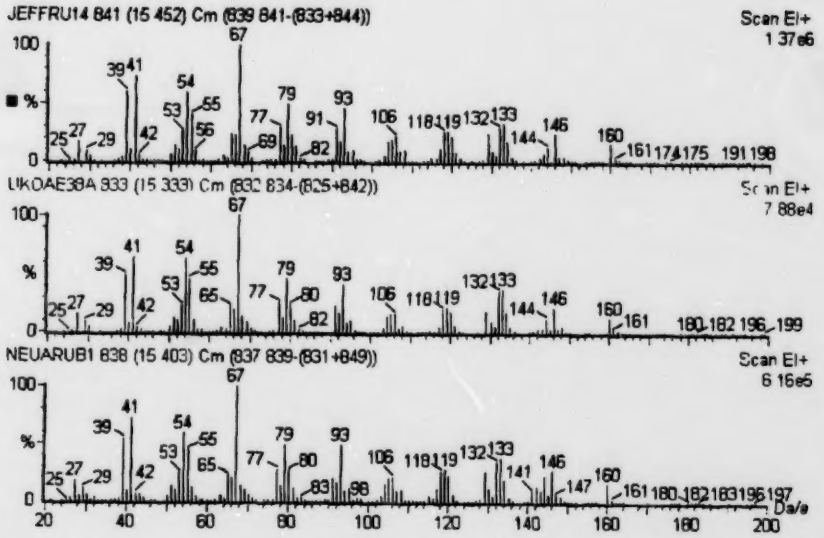


Fig 9 Mass spectra of the compounds giving rise to peak 5 in pyrograms of the three rubbers shown in Fig 4

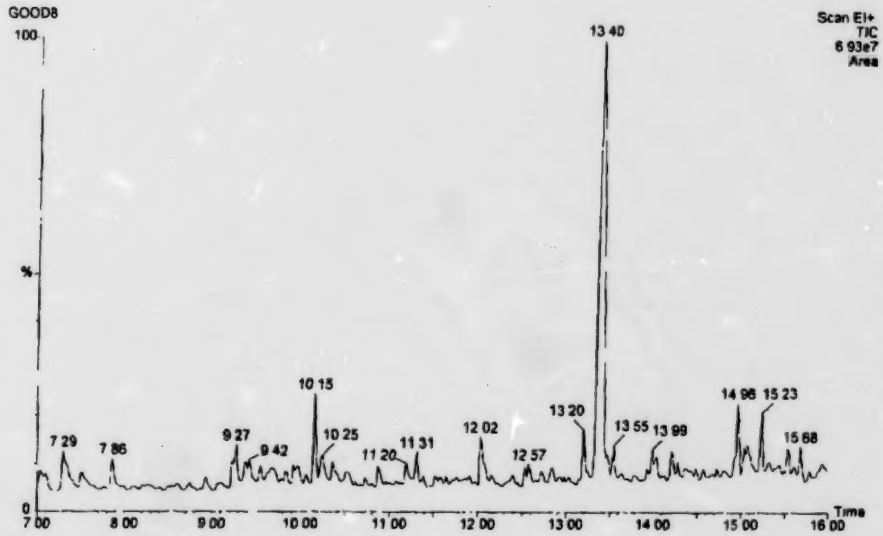


Fig 10 Pyrogram of unknown rubber sample from fuel hose

NBR rubber were present in the sample. The mass spectra of the five compounds are shown in Fig. 11. The difference in the retention times of the five compounds compared to those for NBR #1, NBR #2, and NBR #3 rubbers is due to a change in the length of the capillary column. The column used for this analysis was 25 m long compared to 30 m for the NBR #1, NBR #2, and NBR #3 rubber samples.

4. Conclusions

A py-GC/MS method for the positive identification of NBR rubbers has been described. The method involves confirming the presence of five compounds in the rubber pyrolysate with molecular weights of 93, 103 (benzonitrile), 107, 119, and 160. As the structure of these compounds can be related to areas of NBR rubber where acrylonitrile and butadiene molecules adjoin, they are characteristic and unique to the pyrolysate of NBR rubber.

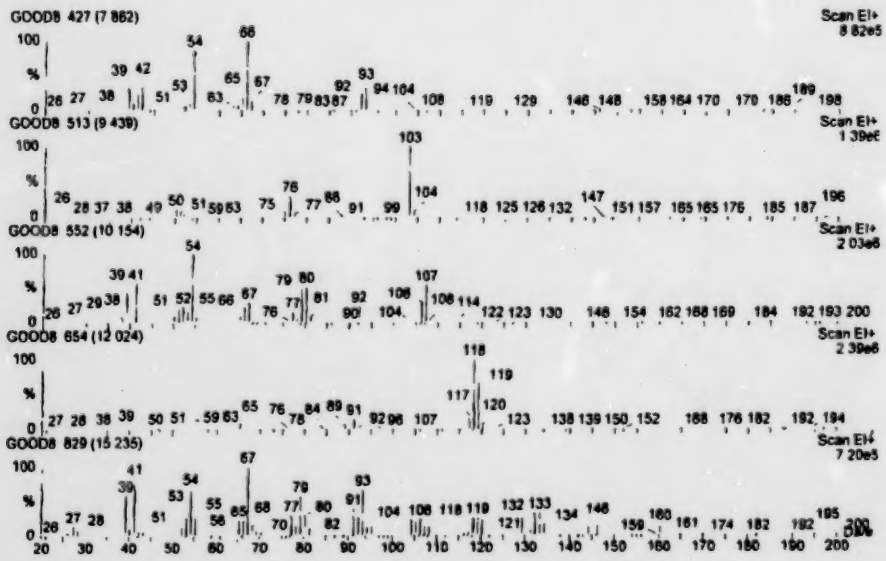


Fig. 11 Mass spectra of compounds characteristic of NBR rubber.

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